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Crystal Structures and Magnetic Properties of the *p*-*N*-Methypyridinium Nitronyl Nitroxide Cation Radical Salts, *p*-MPYNN•I and *p*-MPYNN•ClO_4

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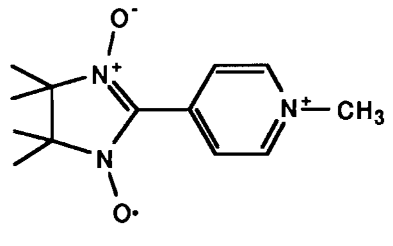
X-Ray crystal analyses and magnetic measurements have been carried out on the *p*-*N*-methylpyridinium α-nitronyl nitroxide (*p*-MPYNN) cation radical salts, *p*-MPYNN•I and *p*-MPYNN•ClO_4. The *p*-MPYNN molecules are connected by short intermolecular contacts between the NO groups in the crystal of *p*-MPYNN•I, while the radical molecules are separated from each other by the ClO_4^- anions in *p*-MPYNN•ClO_4. The magnetic properties of *p*-MPYNN•I and *p*-MPYNN•ClO_4 are found to be consistent with their crystal structures.



p-MPYNN

A radical family, α-nitronyl nitroxide, is attracting interests from the view point of organic/molecular ferromagnetism.[1-7] Recently we have initiated a study of *N*-alkylpyridinium α-nitronyl nitroxide cation radical salts. We have already reported that some of them possess ferromagnetic properties,[8,9] while the iodide salt of 2-(4-*N*-methylpyridinium)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-*N*-oxide (or *p*-*N*-methylpyridinium α-nitronyl nitroxide iodide; abbreviated as *p*-MPYNN•I) shows an exceptionally strong antiferromagnetic intermolecular interaction.[10] It is important to examine the factors in solid state giving not only ferromagnetic couplings but also antiferromagnetic ones. In this letter, we report the crystal structure of *p*-MPYNN•I. Furthermore, we describe the crystal structure and magnetic property of *p*-MPYNN•ClO_4. A large difference has been seen between the two *p*-MPYNN salts.

p-MPYNN•I was prepared by the *N*-alkylation of *p*-pyridyl α-nitronyl nitroxide.[10] The single crystals were obtained by recrystallization from the acetone solution of *p*-MPYNN•I. The I^- anion was easily replaced by ClO_4^-; addition of the equivalent of $AgClO_4$ into the acetone solution led to the immediate precipitation of AgI. After filtration, polycrystalline *p*-MPYNN•ClO_4 was obtained by evaporation. The single crystals were grown from the acetone solution.

p-MPYNN•I crystallized into the triclinic $P\bar{1}$ space group.[11] Figure 1 shows a view of the crystal structure of *p*-MPYNN. The crystal consists of two kinds of intermolecular contacts. The molecules (i) and

(ii) in Fig. 1 are related by inversion symmetry, and have a short contact between the NO groups which could be realized by the Coulombic attraction force between the $N^{\delta+}$ and $O^{\delta-}$ atomic sites. The molecules (i) and (iii) are related by the translational operation along the [110] direction, and there is a short contact between the O-atoms. The former contact makes a radical dimer, while the latter one forms a linear molecular chain. The SOMO[12] is formed by anti-bonding combination of the two π^* orbitals of the NO groups, and is localized on the two NO groups.[2,10] The intermolecular contact between the NO groups means the direct overlap between the SOMOs, which is considered to result in an antiferromagnetic interaction.[2] Therefore, antiferromagnetic couplings are expected in both the intermolecular interactions between (i) and (ii), and between (i) and (iii). The I^- anions are located on the special positions, (0, 0, 0) and (0, 0, 1/2).

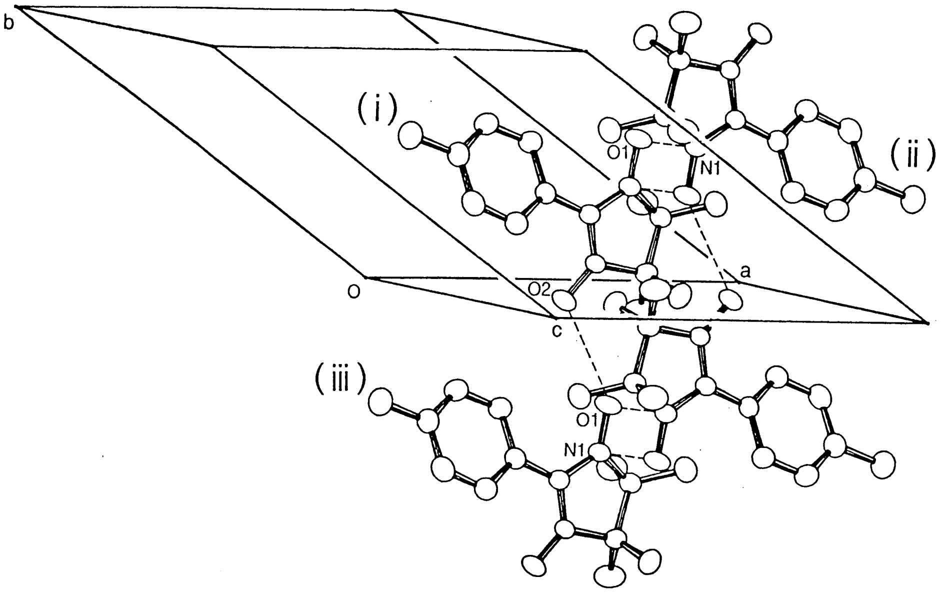


Fig. 1. Crystal structure of *p*-MPYNN•I (Symmetry operations; (i) x, y, z; (ii) -x, -y+1, -z-1; (iii) x-1, y-1, z). Interatomic distances: $O1^{(i)}...N1^{(ii)}$, 3.383(8); $O2^{(i)}...O1^{(iii)}$, 3.159(8) Å.

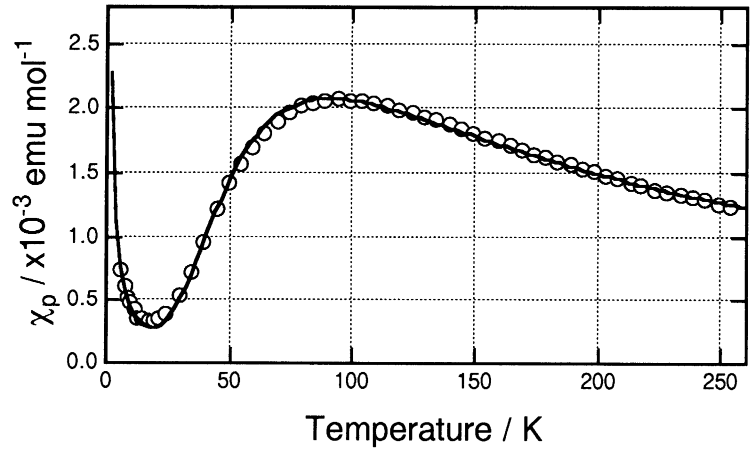


Fig. 2. Temperature dependence of the paramagnetic susceptibilities of *p*-MPYNN•I (from Ref. 10). The solid curve is the theoretical fit (see the text).

Figure 2 shows the temperature dependence of the paramagnetic susceptibilities, χ_p, of *p*-MPYNN•I, reported in ref. 10 previously. We have re-interpreted it, referring to the crystal structure determined in this work. It was found that χ_p of *p*-MPYNN•I can be interpreted in terms of the modified singlet-triplet model,

$$\chi_p = \frac{N_A g^2 \mu_B^2}{k_B(T-\theta)} \frac{\exp(-2J_{AF}/k_B T)}{1+3\exp(-2J_{AF}/k_B T)} + \frac{C_{def}}{T} \tag{1}$$

where $2J_{AF}$ is the antiferromagnetic coupling constant in the dimer, θ is the Weiss constant caused by the weak magnetic interaction between the dimers, and the term C_{def}/T is for the fitting to the Curie behavior appearing below 15 K which could be due to the lattice defects. The solid curve in Fig. 2 is the theoretical best fit, obtained with the parameters, $2J_{AF}/k_B=145$ K, $\theta=-2.7$ K, $g=2.0065$ (fixed), and $C_{def}=0.0046$ emu K mol^{-1}. It was not possible to interprete the temperature dependence in terms of the antiferromagnetic linear chain with a weak antiferromagnetic interchain coupling. These analyses indicate the presence of antiferromagnetic dimers; the antiferromagnetic coupling between the molecules (i) and (ii), should be much larger than that between (i) and (iii). This could be caused by the fact that the SOMO of the molecule (i) spreads not in the direction of the molecule (iii) but the molecule (ii).

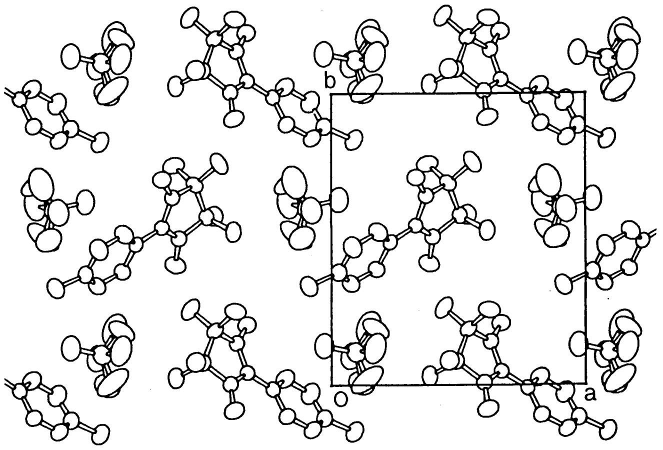


Fig. 3. Crystal structure of *p*-MPYNN•ClO$_4$, projected onto the *ab* plane.

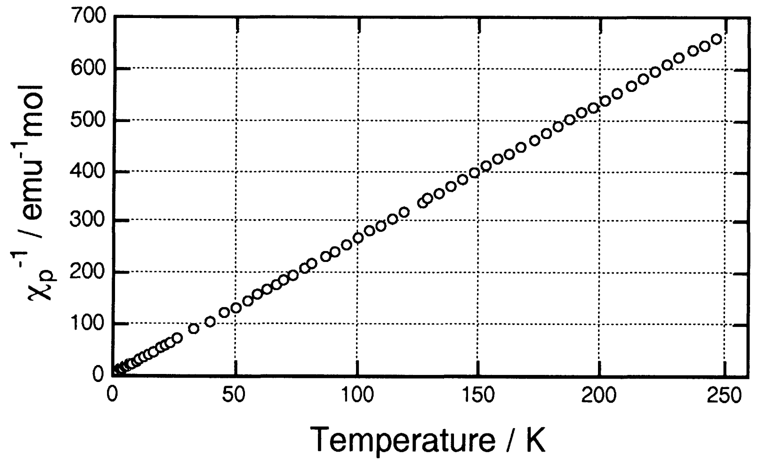


Fig. 4. Temperature dependence of the reciprocal paramagnetic susceptibilities of *p*-MPYNN•ClO$_4$.

p-MPYNN•ClO_4 crystallized into the $P2_1$ space group.[13] Figure 3 shows the projection of the structure onto the *ab* plane. An orientational disorder of ClO_4^- is found around one Cl-O bond. There are short contacts between the pyridinium ring and ClO_4^-, which would be caused by the Coulombic attraction force. Each *p*-MPYNN molecule is separated by ClO_4^-, suggesting a weak intermolecular magnetic interaction. It is worth noting here that this is the first case that the solid state structure is free from dimerization among the crystals of *N*-alkylpyridinium α-nitronyl nitroxides. Figure 4 shows the temperature dependence of the reciprocal paramagnetic susceptibilities of *p*-MPYNN•ClO_4. It follows the Curie-Weiss law with a negative Weiss constant of θ=-1.5 K in the whole temperature range between 3 and 260 K. The weak magnetic interaction in *p*-MPYNN•ClO_4 is consistent with the crystal structure.

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11) Crystal data for *p*-MPYNN•I, triclinic, $P\bar{1}$, a=11.847(7), b=12.695(7), c=9.532(2) Å, α=95.53(5), β=90.55(5), γ=146.89(2)°, V=768.3(8) Å^3, Z=2, R=0.0346, R_w=0.0344. Total 3056 independent reflections with $I>3\sigma(I)$ were used.
12) Singly occupied molecular orbital.
13) Crystal data for *p*-MPYNN•ClO_4: monoclinic, $P2_1$, a=11.013(1), b=12.152(2), c=6.247(1) Å, β=102.03(1)°, V=817.7(2) Å^3, Z=2, R=0.0445, R_w=0.0440. Total 1649 independent reflections with $I>3\sigma(I)$ were used.

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